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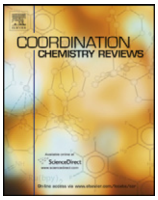

Review

Concepts for metal complex chromophores absorbing in the near infrared

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Contents

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ABSTRACT

The near-infrared (750–2500 nm) region of the electromagnetic spectrum has received enhanced attention recently from the areas of atmospheric and analytical chemistry, from communications technology, and from the side of medical applications. Coordination compounds absorbing strongly in this region can do so because of extended ligand π systems, mixed valency, or the presence of radical ion ligands. The background of such low-energy absorptivity is provided, together with examples from the inorganic and organometallic coordination chemistry of Mo, Mn, Fe, Ru, Os, Rh, Ir, Pt and Cu.

1. Introduction, purpose and scope

The near-infrared (NIR) region of the electromagnetic spectrum, usually defined between 750 and about 2500 nm (14000–4000 cm^{-1}) was discovered by the German–British scientist Friedrich-Wilhelm (Sir Frederick William) Herschel (1738–1822) in 1800. Its association with heat (“calorific rays”) gave rise to one of the contemporary uses of this kind of radiation. However, in recent years the near infrared has become of additional interest in quite diverse areas [1–9]:

- In atmospheric chemistry, the NIR absorption of “greenhouse gases” is responsible for the global heat balance and temperature, and the increasing anthropogenic release of such substances is causing worldwide concern over their climatic consequences.
- In astronomy, near-infrared spectroscopy can be used for searching potentially life-sustaining molecules on planets and for studying the origin of galaxies [2].
- Since much of the solar radiation reaching the surface of the earth lies in the NIR region there is a continuing interest in developing NIR dyes as sensitizers for solar cells [3].
- Glass fibre efficiency in communications technology as recently honoured through the Nobel Prize in Physics (Charles K. Kao, 2009) is possible mainly due to the attenuation minimum of pure silica in certain NIR bands such as the 1300–1350 and 1500–1600 nm regions. The low cost of NIR irradiation sources has also contributed to their use in liquid crystal devices [4] and other systems designed for optical signal processing (e.g. switching, wavelength conversion, memory) [1,5,6].
- NIR spectroscopic analysis of food and related biological materials has become an indispensable and efficient technique in process monitoring and quality control [7]. Analysis of complex probes via NIR spectroscopy requires typically chemometrical methods but no special sample preparation.
- Medical applications of NIR radiation make use of the partial transparency of tissue at such wavelengths and include diagnostics aspects (e.g. non-invasive thermal or biological imaging [8]) as well as therapy (“photodynamic therapy” [9]).

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From the above it follows that NIR dyes are sought-after materials, and coordination compounds such as the well established [4,10,11] dithiolene complexes are one class of substances which can offer absorption and emission activity in that spectral region.

A major purpose of this article is therefore to familiarize coordination chemists (and others) with different concepts to achieve NIR absorptivity of metal complexes. Although this overview cannot be comprehensive or go into detailed discussions of individual electronic structures, both the potential areas of application and the situations leading to NIR absorbing coordination compounds will be mentioned. Not all examples (e.g. classical mixed-valent complexes) and methods (e.g. spectroelectrochemistry) will be treated in full depth in this review because such treatments are available in the literature and are cited. Using instructive examples, the methodology to analyze NIR absorptivity is being discussed for selected cases of inorganic and organometallic coordination compounds of groups 6–11. The main approaches to achieve NIR absorption in the examples discussed are (i) coordination by radical ligands [12], (ii) metal–metal mixed valency [13–17] and (iii) combinations between (i) and (ii).

2. Absorption and absorption measurement in the near infrared (NIR) region

Absorption in the NIR region is typically – but not always – based on molecular overtone and combination vibrations. The OH group is featuring prominently in this respect which explains in part the analytical value of NIR spectroscopy.

Electronic (i.e. non-vibrational) transitions in the near infrared are restricted to a few cases:

- It has long been known that the f block elements can exhibit low energy absorption (and emission) in the NIR region, however, the intensities of absorptions from (forbidden) f–f transitions are inherently low [18].
- On the other hand, large extended organic π systems, with or without metal or other coordination, have typically narrowed HOMO-LUMO gaps and may thus exhibit intense long-wavelength absorption due to allowed low-energy π–π* transitions [5,8,19].
- Small HOMO–LUMO gaps are also known to result from low-energy metal-to-ligand or ligand-to-metal charge transfer (MLCT, LMCT) situations [20] where the barrier for ground state electron transfer between metal and ligand is high enough to prevent intramolecular redox reactivity.

The two additional strategies discussed here which can lead to coordination compounds with strong NIR absorption involve

(i) metal complexes containing (ion) radical ligands, displaying low-energy shifted MLCT, LMCT or intra-ligand (IL) π–π* bands, and
(ii) mixed-valent oligometal or oligo-ligand complexes, i.e. systems with potentially low-energy inter-valence charge transfer (IVCT). Involving metals it is known as metal-to-metal charge transfer (MMCT) [13–16], involving ligands it is referred to as ligand-to-ligand IVCT (LLIVCT, see Chapter 7). Equilibria situations involving metal and ligand have become known as valence tautomerism.

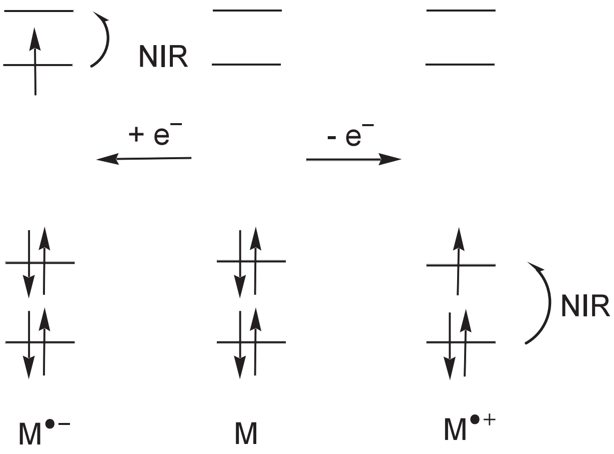
A combination of situations (i) and (ii) is possible and will be discussed here, and the ambivalence between the alternatives (i) and (ii) is a further topic of this overview.

The intermediate character of radicals and radical ions and of mixed-valent species often engenders their production and initial analysis by electrolytic processes, even if they can be obtained also by non-electrochemical means. The technique of spectroelectrochemistry [21], i.e. the combination of energy- and mechanism-focussed electrochemistry with species-specific spectroscopy, has thus been of particular value in the near infrared region [22], the substrates including molecular and macromolecular systems from organic, biochemical, organometallic or inorganic chemistry. Introductions and review collections of topics relevant to this article have appeared recently [23].

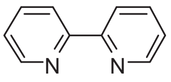
3. NIR absorption by radical ions and their metal complexes

Stable organic molecules in their singlet ground states are usually characterized by large HOMO–LUMO gaps, restricting absorption to the UV and sometimes visible spectral region. One-electron oxidation (to radical cations) or reduction (to radical anions) creates singly occupied molecular orbitals (SOMOs) which offer a potential for low-energy transitions and, in many instances, for corresponding NIR absorption. Fully occupied MOs lying close to the SOMO (former HOMO) in radical cations may thus provide the origin for low-energy transitions to the SOMO whereas empty molecular orbitals lying near the half occupied SOMO (former LUMO) in radical anions may serve as target for low-energy transitions originating from the SOMO (Scheme 1). The propensity for low-energy absorptions by radical ions in particular has been noted before and corresponding spectra and data collections have appeared [24].

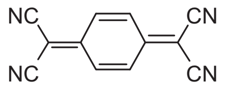
It is therefore not unexpected that radical ions of extended π systems (e.g. conjugated cyanine chains and macrocycles such as phthalocyanines or porphyrins, fullerenes) exhibit NIR absorptions from π–π* transitions [5,8,14,19]. Two examples concerning smaller molecules but potential ligands for metal coordination are the radical anions of 2,2′-bipyridine [25] or similar aromatic α-diimines [26,27] and the one-electron reduced 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) [28]. 2,2′-Bipyridine (bpy) and 2,2′-bipyrimidine (bpym) radical anions have typically weak, vibrationally structured bands at 800–900 nm [25–27] which persist in shifted form after metal coordination [25,26,29] while the $TCNQ^{\bullet -}$ chromophore is distinguished by a strong, asymmetrical band system around 800 nm [28], shifted again after metal binding [30,31] (cf. below). Incidentally, the original π → π* intra-ligand transitions in the neutral ligands usually shift to higher energies in the reduced radical state.



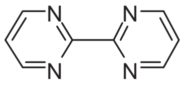
Scheme 1. Near-infrared absorption of radical ions.



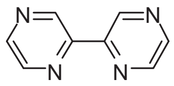
bpy



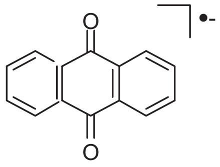
7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ)



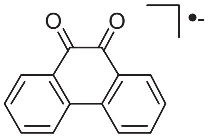
bpym



bpz



I



II

Coordination of metal species to these ions, especially to anions [12], has been observed in the form of ion pairs or ion aggregates or radical ion complexes [32,33]. The perturbation by metal binding and the introduction of additional participating orbitals in the frontier orbital region can create further opportunities to produce low-energy transitions leading to NIR absorption. Such examples have been observed for semiquinones where ruthenium(II) complexes in particular give rise to NIR absorptivity [6,34,35], for certain dicopper(I) complexes of radical anion ligands containing the azo group [36], and for platinum(II) complexes [37a] of one-electron reduced α-diimine ligands such as 2,2′-bipyrazine [37b] (see Fig. 1). Among the quinones, the 9,10-anthrasemiquinone (**I**) and 5,6-phenanthrenesemiquinone (**II**) derivatives have been found to exhibit NIR absorptions, not only as metal-free species [1,24] but also as coordination compounds, while still retaining the radical ligand character despite the presence of redox-active ruthenium [38]. The assignments of such features as shifted IL or MLCT transitions is not always straightforward, especially in those cases where other alternatives such as IVCT transitions in potentially mixed-valent systems of higher nuclearity are conceivable [39]. For paramagnetic species, the EPR method may be most useful to ascertain the electronic structure, as described below for ruthenium complexes of quinonoid ligands and of TCNQ derivatives (Chapter 5.1). The occurrence of NIR absorptions resulting from LLIVCT (ligand-to-ligand IVCT) transitions [40,41] in situations such as $(L^{\bullet-})$–M–(L^{2-}) will also be discussed later (Chapter 7).

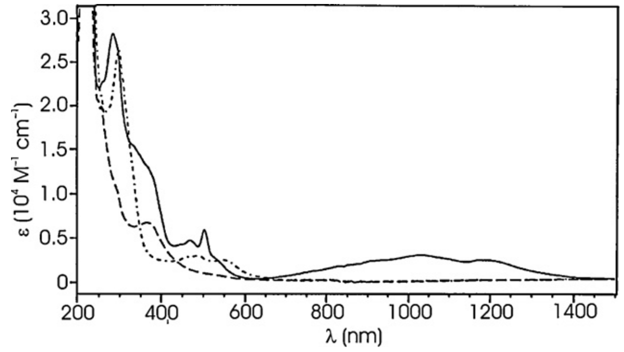
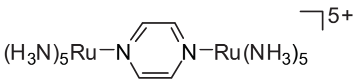


Fig. 1. Absorption spectra of $[Pt(bpz)Mes_2]^n$, bpz = 2,2′-bipyrazine and Mes = mesityl, in THF/0.1 M Bu_4NPF_6 [37a]: *n* = 0 (– –), *n* = 1– (···), *n* = 2– (—).

4. NIR absorption by mixed-valent systems

The long-wavelength absorption capacity of mixed-valent species has been recognized for centuries, e.g. in the form of the strong VIS-to-NIR absorption [42] of Prussian Blue, simply formulated as $\{Fe^{III}_4[Fe^{II}(CN)_6]_3\}$. The understanding of these and related colour phenomena was then systematically developed in the seminal article by Robin and Day [13], expanded later in the field of coordination chemistry by Creutz [14], Crutchley [15], Meyer and coworkers [16]. The initially limited selection of examples has been expanded more recently [17,43].

On a basic level, the low-energy transitions in compounds containing an element in two different neighbouring oxidation states may be described as resulting from the charge transfer between communicating electron-rich (donor) and electron-deficient (acceptor) centers. This description of the localized case (weak coupling) may be extended to a strongly coupled, delocalized situation with small or vanishing barrier for intramolecular electron transfer where the transitions then occur between related occupied and unoccupied MOs following orbital interaction [14]. While the low-energy absorption in the NIR region is often the result of weak-to-moderate interactions between formally equivalent sites such as in the celebrated Creutz-Taube ion **III** [14,44], the intensity of such rather variable (cf. below) inter-valence transitions is determined by the orbital overlap [13–16].

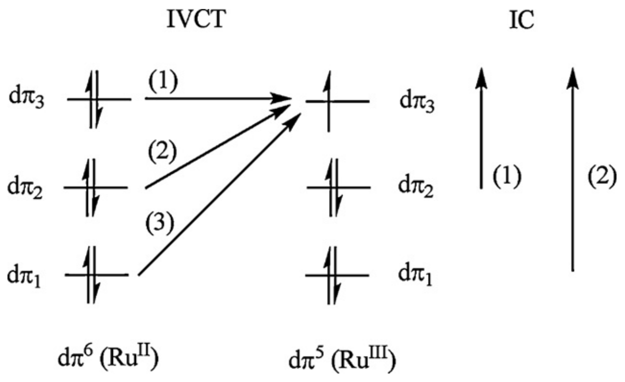


III

Depending on the electronic configuration, one or more transitions may be expected to occur in the NIR or even mid-infrared region, as sketched in Scheme 2 [16] for the classical d^6/d^5 system by example of **III** (λ_{max} = 1570 nm, ε = 5000 $M^{-1}\,cm^{-1}$, $\Delta\nu_{1/2}$ = 1250 cm^{-1}) [44].

The scope of variations of NIR absorptivity from IVCT transitions relative to the benchmark case of the Creutz-Taube ion **III** is illustrated by the following examples:

Replacement of the neutral donors NH_3 in the periphery by the anionic π acceptors CN^- in $[(NC)_5Ru(\mu\text{-pz})Ru(CN)_5]^{5-}$ (**IV**), pz = pyrazine, causes a decreased electrochemical stability constant K_c and a broadened NIR absorption (Fig. 2) from the IVCT transition [45]. This probably reflects a more localized valence situation caused by weakened Ru–pz–Ru cross-coupling as a result



Scheme 2. IVCT and IC (interconfigurational) transitions in d^6–d^5 mixed-valence systems such as Ru^{II}–L–Ru^{III} complexes (modified from ref. [16b]).

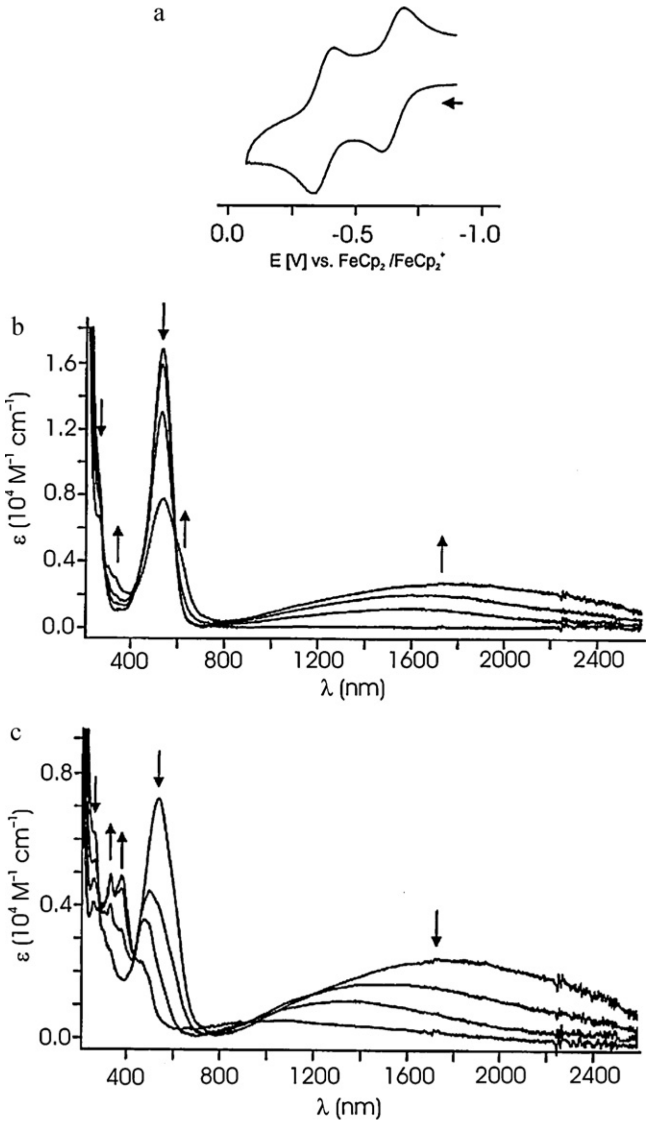
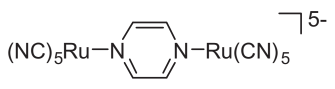


Fig. 2. Cyclic voltammogram (a) and stepwise UV–Vis-NIR spectroelectrochemical oxidation (b,c) of $[(NC)_5Ru(\mu\text{-pz})Ru(CN)_5]^{6-}$ in CH_2Cl_2/0.1 M Bu_4NPF_6 (modified from Ref. [45]). The broad NIR band is exclusive to the (5−) intermediate (**IV**).

of competition from both kinds of acceptors (cyanide, pyrazine bridge) for the electrons of ruthenium.



IV

Changing the metal from ruthenium to iron in $[(NC)_5Fe(\mu\text{-pz})Fe(CN)_5]^{5-}$ (**V**) leads to a low-energy shift (Fig. 3) following from weakened metal-metal interaction (3d–3d vs. 4d–4d situation) [46]. Less efficient dπ–π*(pz) overlap is made responsible for this difference. Both UV–Vis-NIR spectrophotometers and FTIR instruments can be used for measurements (Fig. 3). An aprotic solvent was chosen because earlier reports from aqueous media [47] did not produce a mixed-valent intermediate with sufficient stability. The cyanide periphery also conveys a particular solvent dependence (solvatochromism) to the IVCT band, as has been studied in detail for the stable analogue $[(NC)_5Fe(\mu\text{-tz})Fe(CN)_5]^{5-}$ (**VI**), tz = 1,2,4,5-tetrazine [48].

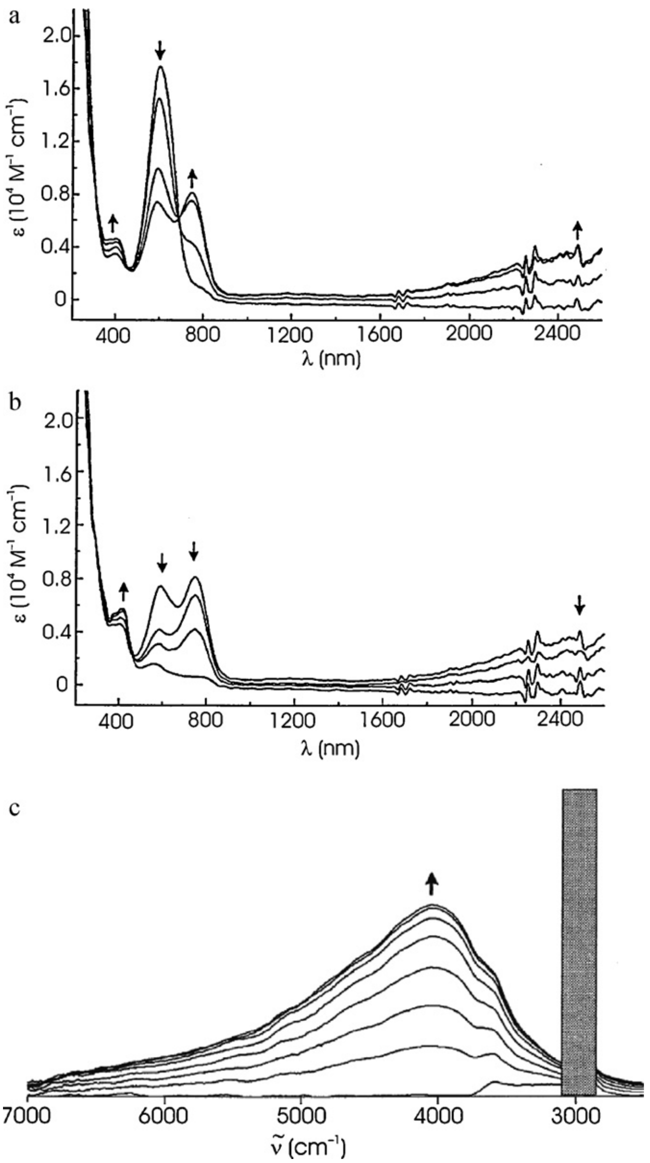
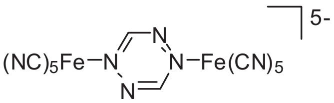


Fig. 3. Spectroelectrochemical oxidation behaviour of $[(NC)_5Fe(\mu\text{-pz})Fe(CN)_5]^{6-}$ in CH_3CN/0.1 M Bu_4NPF_6 recorded on a UV–Vis-NIR spectrophotometer (two one-electron steps (a) and (b)), and on an FTIR instrument (first step (c); modified from Ref. [46]). The NIR band is exclusive to the (5−) intermediate (**V**).



VI

Although **VI** is clearly a diiron(2.5) species [49], its IVCT band in the NIR region is not solvent insensitive as is often postulated [14] for valence-averaged mixed-valent systems due to the absence of a permanent dipole moment.

- Organometallic analogues $[(R_3P)_2(OC)_3M(\mu\text{-pz})M(CO)_3(PR_3)_2]^+$ (**VII**) M = Mo or W, of the Creutz-Taube ion **III** could be produced spectroelectrochemically to exhibit intense ($\varepsilon \approx 5000\ M^{-1}\ cm^{-1}$) symmetrical NIR bands around 2100 nm [50]. Their IR vibrational spectra, especially the CO stretching bands, reveal valence delocalization (average oxidation state + 0.5) in CH_2Cl_2 solution on the time-scale of the IR experiment (10^{-13} s [51]).

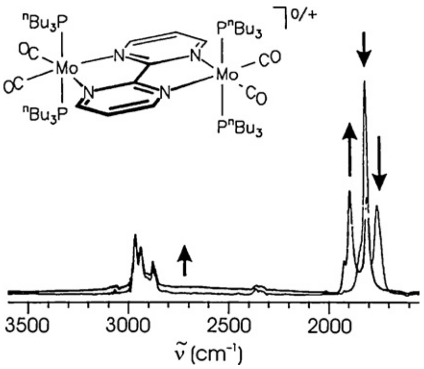
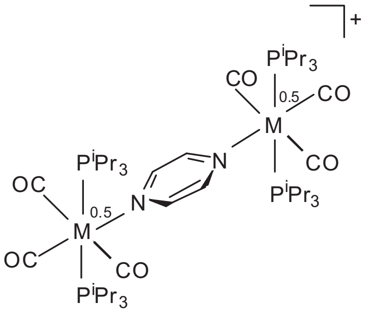


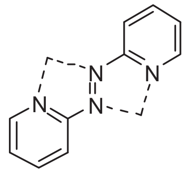
Fig. 4. IR-spectroelectrochemical oxidation $[(R_3P)_2(OC)_2Mo(\mu\text{-bpym})Mo(CO)_2(PR_3)_2]^{(o)->(+)}$, R = *n*-butyl, in CH_2Cl_2/0.1 M Bu_4NPF_6, revealing a weak broad band for an IVCT electronic transition of the cation **VIII** overlapping with the narrow vibrational absorption bands (modified from Ref. [52]).



VII

- A closely related example, $[(R_3P)_2(OC)_2Mo(\mu\text{-bpym})Mo(CO)_2(PR_3)_2]^+$ (**VIII**), shows the enormous variation in NIR band appearance from IVCT transitions. This $(Mo^{0.5})_2$ system [52] has a very weak electronic absorption around 2700 cm^{-1} (3700 nm, Fig. 4) as a consequence of the different metal/ligand orbital overlap in a bis-chelate situation [53].

The low IVCT band intensity in such bis-bidentate chelate arrangements was discussed recently [43], it is evident also for diruthenium, diosmium and Ru/Os metal mixed-valent complexes **IX** [54] with the bridging ligand 2,2′-azobispyridine (abpy, [2,2′-(1,2-diazenediyl-κN1:κN2)bis[pyridine-κN]]; see Fig. 5 [55,56]) which will also feature later in this contribution.



2,2′-azobispyridine (abpy)

Spectra A and C show weak IVCT absorptions from emerging symmetrical mixed-valent forms in the near infrared, for the unsymmetrical Ru^{II}/Os^{III} complex (B) this MM′CT transition is shifted to higher energies. The osmium containing compounds (B,C) exhibit triplet MLCT transitions for the non-oxidized states in the NIR region.

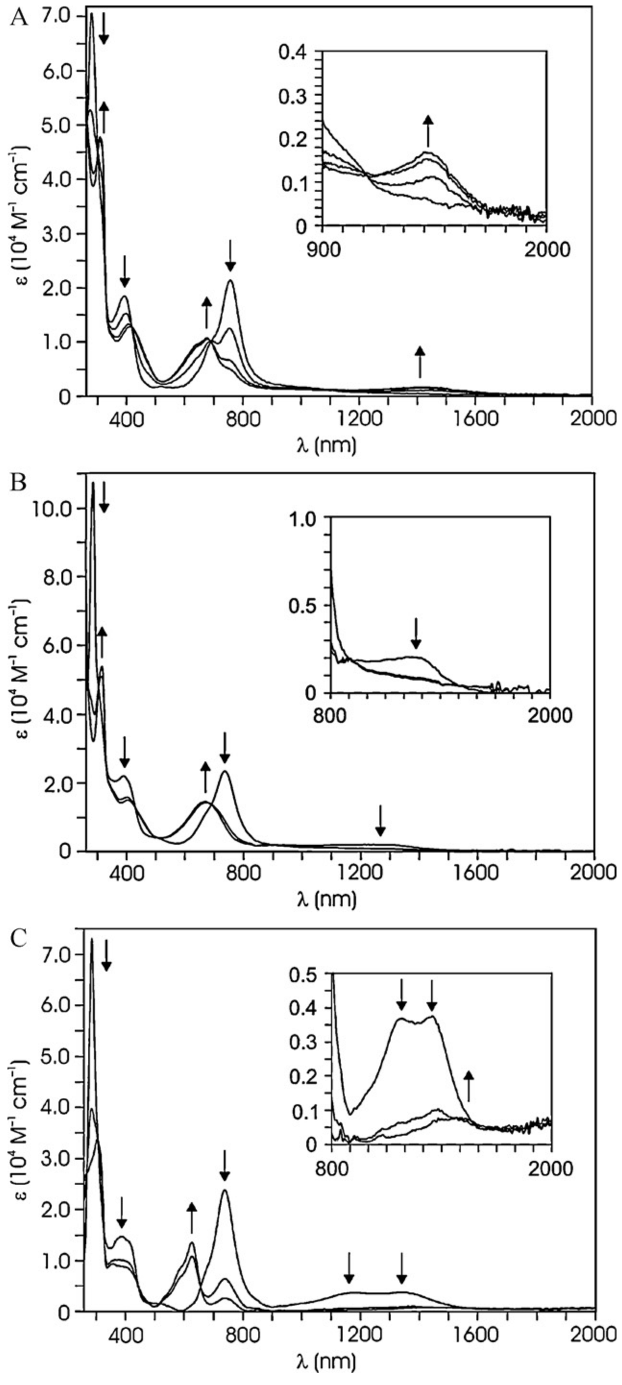


Fig. 5. UV–Vis-NIR Spectroelectrochemical behaviour of complex ions $[(bpy)_2M(\mu\text{-abpy})M'(bpy)_2]^{4+}$ on one-electron oxidation to (5+) ions **IX** in CH_3CN/0.1 M Bu_4NPF_6 (modified from ref. [54]): (A) M,M′ = Ru; (B) M = Ru, M′ = Os; (C) M,M′ = Os (NIR regions in the insert).

Most studies of mixed valency in coordination compounds have focussed on d^6/d^5 systems, especially on $Fe^{II}Fe^{III}$ and $Ru^{II}Ru^{III}$ combinations. The prevalence of Fe^{II}/Fe^{III} and Ru^{II}/Ru^{III} species in mixed valence research is related to the significance of iron and ruthenium in biochemistry and catalysis, to the thermodynamic stability of both the +II and +III oxidation states of these elements, and to the convenient redox potentials for +II/+III conversion. While ruthenium complexes are further stabilized kinetically to form especially very inert Ru–N bonds, the advantage of iron compounds is to have Mössbauer spectroscopy on disposal for spin and oxidation state determination.

In addition to d^6/d^5 there are other d electron configuration arrangements which can be responsible for NIR absorption. Using a bis-chelating pyrazine derivative 2,5-bis(1-phenyliminoethyl)pyrazine (bpip) as bridge and organometallic

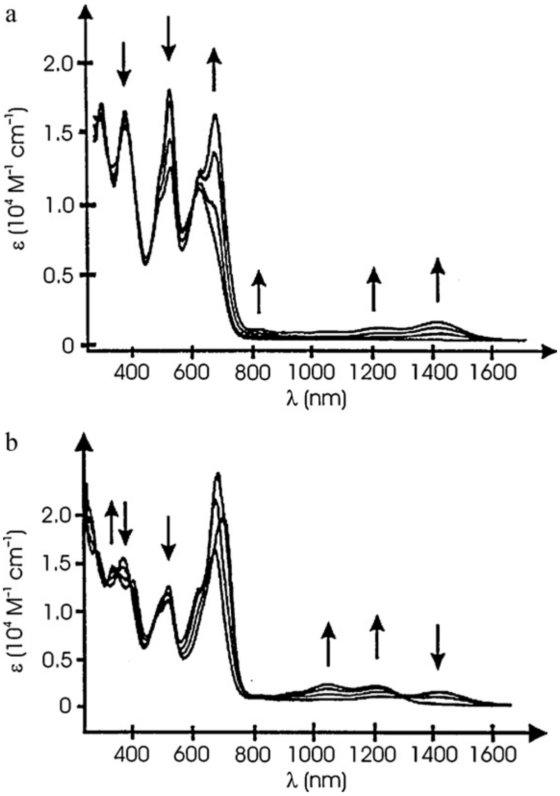


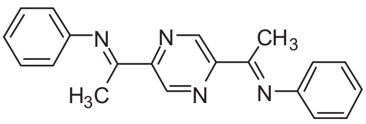
Fig. 6. UV–Vis-NIR Spectroelectrochemical behaviour of the electrogenerated complex ion $[(C_5Me_5)ClIr(\mu\text{-bpip})Ir(C_5Me_5)]^+$ on stepwise one-electron reduction to $[(C_5Me_5)Ir(\mu\text{-bpip})Ir(C_5Me_5)]^+$ (**X**) (EC process, (a)) and then to $[(C_5Me_5)Ir(\mu\text{-bpip})Ir(C_5Me_5)]$ (b) in DMF/0.1 M Bu_4NPF_6. The mixed-valent character of the intermediate **X** (M = Ir) is confirmed by EPR (modified from ref. [57]).

complex fragments of rhodium or iridium, it has been possible to produce spectroelectrochemically the mixed-valent intermediate $[(C_5Me_5)M(\mu\text{-bpip})M(C_5Me_5)]^+$ (**X**), M = Rh or Ir, which contain M^{II} (d^7) and exhibit sizeable *g* anisotropy in the EPR spectra and clearly detectable NIR absorptions at 1200–1700 nm (Fig. 6) [57].

$$\begin{tikzcd}[(C_5Me_5)ClM(\mu\text{-bpip})MCl(C_5Me_5)]^{2+} + 2\,e^- \arrow[r] & {[(C_5Me_5)ClM(\mu\text{-bpip})M(C_5Me_5)]^+ + Cl^-} \arrow[d, "-Cl^-"', "+1\,e^-"] \\ & {[(C_5Me_5)M(\mu\text{-bpip})M(C_5Me_5)]^+}\end{tikzcd}$$

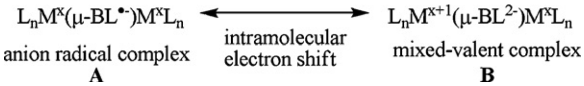
X

This example illustrates how electron transfer coupled with chemical reactivity (e.g. bond formation or breaking) can lead to NIR absorbing intermediates where they may not be expected [58].



bpip

- In addition to π acceptors such as pyrazine and its derivatives there are also π donor bridges suitable to mediate electronic interaction between inorganic or organic moieties in mixed oxidation states. An example is the dimanganese(1.5) complex $[(C_5H_4Me)(OC)_2Mn(\mu\text{-im})Mn(CO)_2(C_5H_4Me)]$ (**XI**) (λ_{max} = 1430 nm in toluene [59]) where im⁻ is the biochemically relevant imidazolate, a symmetrical σ and π donating bridge.



Scheme 3. An ambivalent three-center situation: (BL = non-innocent bridging ligand).

im⁻

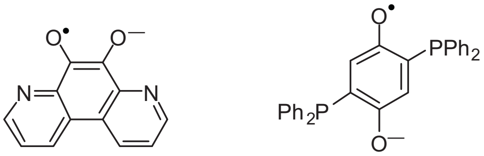
- In addition to homodinuclear complexes with equivalent metal sites there are heterodinuclear systems conceivable with IVCT-like MM'CT (metal(1)-to-metal(2) charge transfer) transitions in the near infrared. The combination between ferrocene/ferrocenium and ruthenium(II/III) has been a well investigated target [60].

5. Ambivalent electronic situations in NIR-active three-center systems M–(μ-L)–M

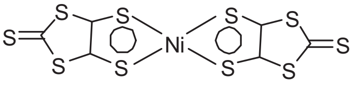
Coordination compounds with several (>1) redox-active transition metals and non-innocent ligands have been of interest due to the ambivalence regarding their proper description [39]. For the prototypical dinuclear case (Scheme 3) the two alternatives of radical bridged homovalent species, **A**, and non-radical bridged mixed-valent arrangement, **B**, can be formulated. The corresponding assignment of NIR absorptions as either IL radical bands or IVCT transitions often requires additional information from crystal structure analysis, IR/Raman vibrational or EPR spectroscopy. Ideally, such experimental information is further complemented by DFT or other calculations.

For instance, the dinuclear *o*- and *p*-semiquinone diruthenium(II) complexes $\{(\mu\text{-BL})[Ru(bpy)_2]_2\}^{3+}$ (**XII**) with NIR absorptions at about 1200 nm were assigned as such [39] on the basis of a small *g* anisotropy of the EPR signal ($1.98 < g < 2.05$) which would not be compatible with significant participation of ruthenium(III) with its high spin–orbit coupling constant [61] at the singly occupied MO. The spin–orbit coupling constant is a major factor in determining the size of the isotropic *g* factor and the range of the *g* tensor components [12].

μ-BL:

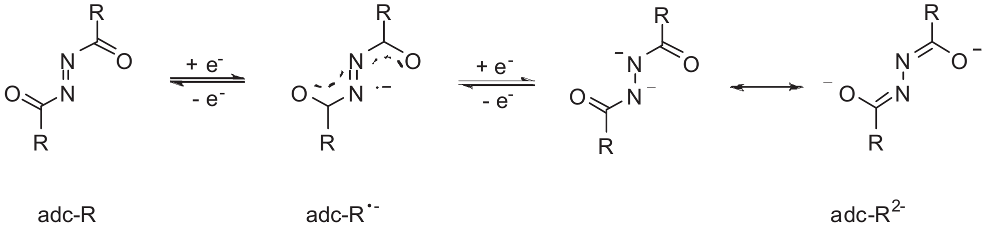


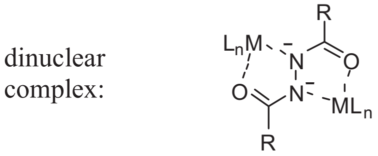
One class of compounds prominent as dyes in the mid-NIR region (up to about 1700 nm) are one-electron reduced bisdithiolene complexes e.g. of nickel [4,10,11], such as **XIII**. These well researched compounds owe their long-wavelength absorption to the electronic delocalization between the partially reduced dithiolenes and the metal d orbitals.



XIII

Such a mixed transition metal/non-innocent ligand situation has also been established [62] for another potentially useful electrochromic system [62,63] involving two ruthenium centers and a non-innocent conjugated bridging ligand system azo-1,2-dicarbonyl (adc-R)/1,2-diacylhydrazido(2-) (adc-R^{2-}).





Compound [(bpy)$_2$Ru(μ-adc-OEt)Ru(bpy)$_2$]$^{3+}$ (**XIV**) was first studied in analogy to the Creutz-Taube ion **III** [64]. A comparison of the corresponding diruthenium and diosmium compounds [(bpy)$_2$M(μ-adc-Me)M(bpy)$_2$]$^{3+}$ revealed a remarkable difference to **III** which was attributed to the π donor character of the partially reduced adc-R bridges in contrast to the π acceptor character of pyrazine [65]. In any case, a two step reversible redox system with electrochromic behaviour, especially with a strongly ($\varepsilon > 7000\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) NIR absorbing intermediate was established.

A most striking observation, however, was made when a series of compounds [(bpy)$_2$Ru(μ-adc-R)Ru(bpy)$_2$]$^{3+}$ (**XV**) with substituents R varying from strong donors NR$_2$ via OR and alkyl groups to acceptors such as 4-carbomethoxyphenyl or CF$_3$ was studied [62,66]. While the NIR absorption of all (3+) species remained in the potentially useful 1600 nm region (see e.g. Fig. 7), the EPR and other data suggested that the character of the intermediate shifted continuously from a radical species with mostly ligand localized spin and small *g* anisotropy to a mixed valent compound with a dianionic bridge, with predominant metal centered spin and large *g* anisotropy [62].

The crystal structure for the precursor [(bpy)$_2$Ru(μ-adc-CF$_3$)Ru(bpy)$_2$]$^{2+}$ of the trifluoromethyl-substituted complex showed a dianionic bridge corresponding to a bis(carbamoyl) species and the metals separated by about 5.0 Å (Fig. 8) [66]. This relatively short distance for a molecule bridged dinuclear complex results from the edge-sharing of the two five-membered chelate rings [56].

The systems [(bpy)$_2$Ru(μ-adc-R)Ru(bpy)$_2$]$^{3+}$ (**XV**) reported by us since 1988 [64] have been used by the group of Zhi Yuan Wang for studies targeted at optical attenuation around 1550 nm as required for wavelength-division multiplexing [35,63]. It was found that the stability of the materials was high (18,000 switching cycles) and that the electrochromophore could be introduced into dendritic and polymeric structures [67]. Electroluminescence as well as photoluminescence were investigated and NIR emission at 790 nm was found for corresponding single-layer diode devices [68,69]. Further recent developments have confirmed the suitability of these coordination compounds as materials in NIR applications [68], and, incidentally, molybdenum complexes have also shown similar behaviour in the near infrared region [6,70]

In an attempt to change the charge of the intermediate from (3+) to (1−) it was possible to synthesize [(acac)$_2$Ru(μ-adc-OR)Ru(acac)$_2$] (**XVI**), R = alkyl and acac$^-$ = acetylacetonate = 2,4-pentanedionato, with a Ru^{III}—Ru^{III} distance of 4.76 Å. This could be reduced to a mixed-valent species [(acac)$_2$Ru(μ-adc-OR)Ru(acac)$_2$]$^-$ (**XVI**$^-$) with intense absorption at $\lambda_{max} = 2000$ nm [71].

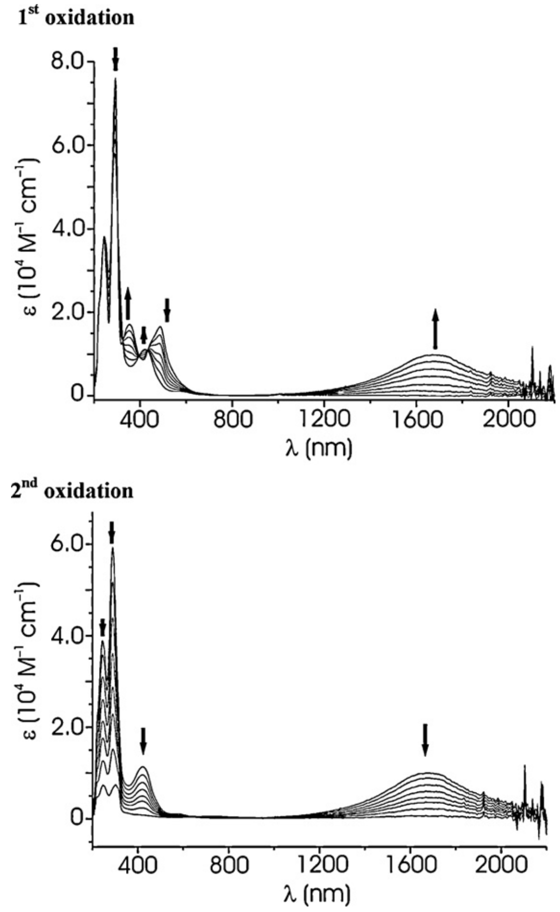


Fig. 7. UV–Vis-NIR Spectroelectrochemical behaviour of [(bpy)$_2$Ru(μ-adc-CF$_3$)Ru(bpy)$_2$]$^{2+}$ on stepwise one-electron oxidation in CH$_2$Cl$_2$/0.1 M Bu$_4$NPF$_6$ (modified from ref. [66]). The NIR band is exclusive to the (3+) intermediate (**XV**).

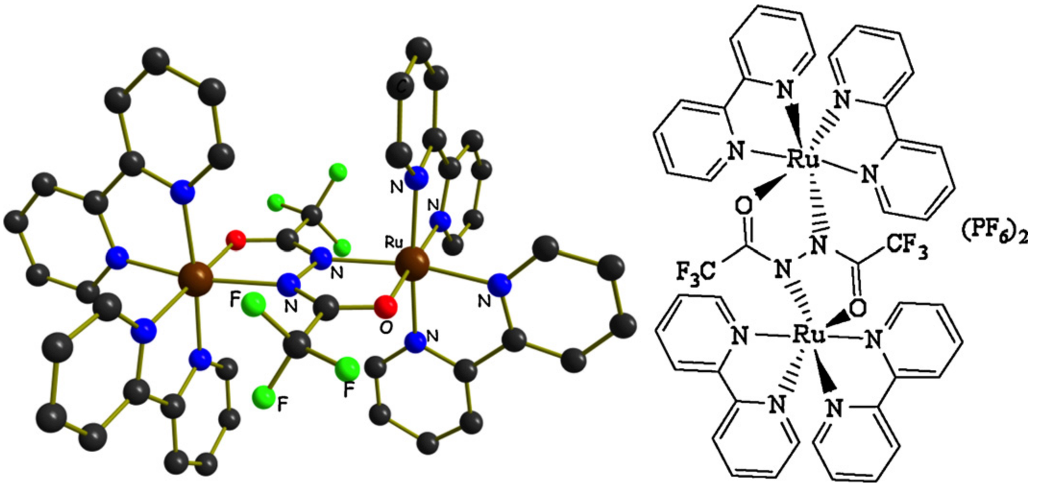
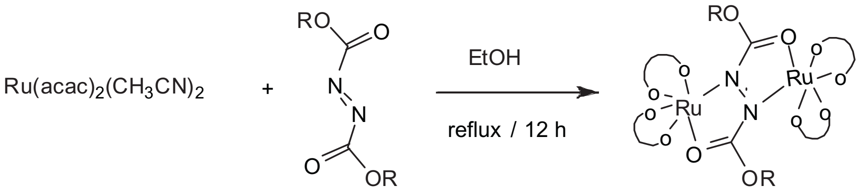


Fig. 8. Molecular structure of the dication in the crystal of $[(bpy)_2Ru(\mu\text{-adc-CF}_3)Ru(bpy)_2](PF_6)_2$ [66].



adc-OR

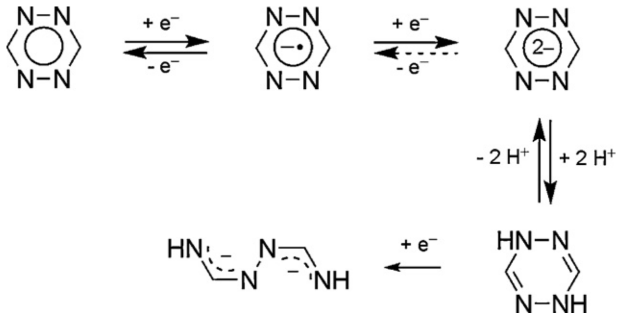
XVI

ΔΛ (meso)
ΔΔ/ΛΛ (rac)

In contrast, the related systems $[(acac)_2Ru(\mu\text{-dih-R})Ru(acac)_2]^-$ (**XVI**) with an all-nitrogen 1,2-diiminohydrazido $(\text{dih-R})^{2-}$ bridge (which was obtained via reductive ring opening of 1,2,4,5-tetrazines [72], Scheme 4) showed ligand-based spin, in spite of the deceptive NIR absorption around 1400 nm [73].

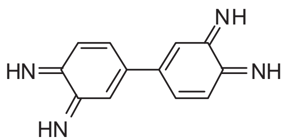
Comparison of these kinds of intermediates with their alternative between the radical ion formulation $Ru^{II}(L^{\bullet-})Ru^{II}$ (**A**) and the $Ru^{III}(L^{2-})Ru^{II}$ mixed-valence description (**B**) (Scheme 3) reveals the following:

The easier reduction of the C=O vs. the C=NH containing bridge (electronegativity !) results in a preference of $[(acac)_2Ru^{II}(\mu\text{-adc-R}^{2-})Ru^{III}(acac)_2]^-$ (**XVI**$^-$) for **B** and of $[(acac)_2Ru^{II}(\mu\text{-dih-R}^{\bullet-})Ru^{II}(acac)_2]^-$ (**XVII**) for **A**. On the other hand, the stabilization of Ru^{II} by π accepting bpy and of Ru^{III} by π donating $acac^-$ results in a substituent dependent ambivalent situation (**A** or **B**) for $[(bpy)_2Ru(\mu\text{-adc-R})Ru(bpy)_2]^{3+}$ (**XV**) whereas $[(acac)_2Ru(\mu\text{-adc-R})Ru(acac)_2]^-$ (**XVI**$^-$) clearly prefers the mixed-valent situation **B**.



Scheme 4. Reductive ring-opening of 1,2,4,5-tetrazines.

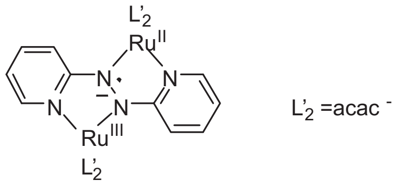
The value of EPR information for assigning NIR absorptions in dinuclear complexes with non-innocent ligands was also made evident for the cation and the anion of the system $\{(\mu\text{-L})[Ru(acac)_2]_2\}^n$ (**XVIII**^{n}) where the neutral form of L is 3,3′,4,4′-tetraimino-3,3′,4,4′-tetrahydrobiphenyl [74]. While the cation (**XVIII**$^+$) with $\lambda_{max} = 1570$ nm ($\varepsilon = 4000\ M^{-1}\ cm^{-1}$) is a $Ru^{II}Ru^{III}$ mixed-valent species according to the wide *g* spread in the EPR spectrum, the anion **XVIII**$^-$ ($\lambda_{max} = 2160$ nm, $\varepsilon = 800\ M^{-1}\ cm^{-1}$) exhibits no detectable *g* anisotropy ($g_{iso} = 2.003$) which indicates an anion radical complex [12] of diruthenium(II) [74].



L

Although the field of coordination compounds with mixed-valence metals has been dominated by d^6/d^5 systems, especially by $Fe^{II}Fe^{III}$ and $Ru^{II}Ru^{III}$ combinations, other d electron configurations can also be involved in mixed valency and produce NIR absorption. Staying with ruthenium, yet in an organometallic form as the widely used [75] (arene)Ru entity, it was possible to generate spectroelectrochemically a mixed-valent intermediate $[(Cym)Ru(\mu\text{-abpy})Ru(Cym)]^+$ (**XIX**), Cym = *p*-cymene = 1-isopropyl-4-methylbenzene, containing Ru^I (d^7) which exhibits sizeable *g* anisotropy and a weak but clearly detectable NIR absorption at about 1500 nm [76].

Very intense NIR absorption at about 840 nm ($\varepsilon = 29{,}000\ M^{-1}\ cm^{-1}$) was observed for both *rac* and *meso* diastereoisomers of the diamagnetic $[(acac)_2Ru(\mu\text{-abpy})Ru(acac)_2]$ (**XX**) [77]. Attributing this absorption to a transition with IVCT character is based on the structural evidence for an anion radical ligand bridge $abpy^{\bullet-}$ (d_{NN} = 1.37 Å) which leaves only a mixed-valent description ($Ru^{II}Ru^{III}$ or, more likely, $(Ru^{2.5})_2$) for the two metals.



The resulting formulation $Ru^{2.5}(\mu\text{-}L^{\bullet-})Ru^{2.5}$ corresponds to what is generally assumed as the excited state description for a symmetrically dinuclear complex undergoing metal/ligand charge transfer (1). Conversely, the intense NIR absorption of the complex $[(acac)_2Ru(\mu\text{-abpy})Ru(acac)_2]$ leads to a homovalent situation in the excited state (2).

$$Ru^{II}(\mu\text{-}L^{o})Ru^{II} \xrightarrow{MLCT} [Ru^{2.5}(\mu\text{-}L^{\bullet-})Ru^{2.5}]^{*} \xleftarrow{LMCT} Ru^{III}(\mu\text{-}L^{2-})Ru^{III} \qquad (1)$$

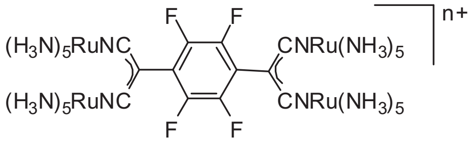
$$[Ru^{II}(\mu\text{-}L^{o})Ru^{II}]^{*} \xleftarrow{LMCT} Ru^{2.5}(\mu\text{-}L^{\bullet-})Ru^{2.5} \xrightarrow{MLCT} [Ru^{III}(\mu\text{-}L^{2-})Ru^{III}]^{*} \qquad (2)$$

Following this interpretation [77], Bonvoisin and coworkers [78] have reported related a case of a mixed-valent arrangement formally bridged by a radical ligand ($\lambda_{max} \approx 1000$ nm).

6. NIR absorption in complexes of higher nuclearity

Mixed valency or radical ligand formation can produce NIR absorption in coordination compounds of higher nuclearity (e.g. tri-, tetra-, or hexanuclear complexes or clusters [79,80], where metal centers may be ligand-bridged or metal–metal bonded.

A remarkable example concerns the tetranuclear ruthenium complexes of TCNQ and its derivatives. Complexes of such strong electron acceptor molecules continue to be applied in the construction of new materials with special optical, electrical and magnetic properties [81,82]. While the radical anion of the free ligand $TCNQ^{\bullet-}$ absorbs already in the NIR at λ_{max} = 842 nm [28], the tetrakis(pentaammineruthenium(II)) compound $\{(\mu_4\text{-TCNQ})[Ru(NH_3)_5]_4\}^{7+}$ (**XXI**) exhibits a similarly asymmetric but bathochromically shifted band system with a maximum at 1560 nm [31a], i.e. within the fibre optics telecommunications band range. EPR spectroscopy confirms the largely ligand centered spin in agreement with a $(TCNQ^{\bullet-})(Ru^{II})_4$ formulation. The use of the even better π accepting 2,3,5,6-tetrafluoro-TCNQ ligand in **XXII**, *n* = 7, reveals a slightly higher metal contribution to the singly occupied MO and an even further shifted NIR absorption at λ_{max} = 1822 nm (Fig. 9) [31b].



XXII

While the spectra of $\{(\mu_4\text{-TCNQ})[Ru(NH_3)_5]_4\}^{7+}$ (**XXI**) and of the tetrafluoro-substituted analogue (**XXII**, *n* = 7) are identified [83] as shifted absorptions known from the free ligand [28], the original non-reduced (8+) ions also have intense near IR absorptivity (Fig. 9) which results from weakly coupled mixed-valent $(Ru^{2.5})_2$ terminal groups (dimer-of-dimers model) [31,83].

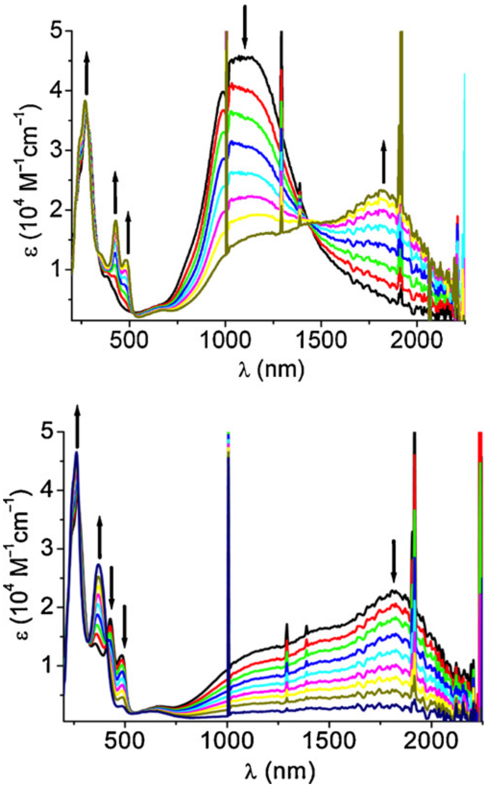


Fig. 9. UV–Vis-NIR spectroelectrochemical reduction $\{(\mu_4\text{-TCNQF4})[Ru(NH_3)_5]_4\}^{(8+)\text{->}(7+)}$ (top) and $\{(\mu_4\text{-TCNQF4})[Ru(NH_3)_5]_4\}^{(7+)\text{->}(6+)}$ (bottom) in $CH_3CN/0.1/Bu_4NPF_6$ [31b].

Near infrared absorption of oligonuclear compounds is not only expected with non-innocent ligands bridging single metal centers but also when metal cluster entities with close-lying frontier orbitals are electronically coupled [80]. Direct metal–metal bonding in discrete and especially polymeric compounds such as $[\{Ru(CO)_2L\}^m]_n$, e.g. *L* = 2,2′-bipyridine [84], is also frequently causing near infrared absorption, reflecting an approach to one-dimensional metallic systems.

7. NIR absorption from mixed-valency of coordinated radical ligands

A further possibility to achieve NIR absorption in coordination compounds with non-innocent ligands arises when two or more such ligands have different oxidation states. In this case a coordination-supported electron transfer between two mixed-valent ligands can produce low-energy electronic ligand-to-ligand inter-valence charge transfer (LLIVCT) transitions. High intensities of corresponding absorptions can be expected if the typical π systems involved are coplanar and if they can interact with d orbitals of the bridging metal.

Examples include the 1,2-dioxolene-type chelate ligands which allow for *o*-quinone (Q), *o*-semiquinone anion ($Q^{\bullet-}$) and catecholate dianion (Q^{2-}) forms. In the simplest possible one-metal/two-ligand arrangement Q–M–Q there are two ligand-ligand mixed-valent possibilities (Q^{o})–M–($Q^{\bullet-}$) and ($Q^{\bullet-}$)–M–(Q^{2-}) and corresponding studies with M = Ni^{II} or Cu^{II} and substituted ligands Q have shown corresponding NIR absorptivity [85,41].

As an example, a copper(II) complex (Q)Cu(Q) (**XXIII**) with two mutually twisted 4,6-di-*tert*-butyl-(2-methylthiophenylimino)-*o*-benzosemiquinone ligands $Q^{\bullet-}$ and moderately intense LMCT bands in the VIS-to-NIR region can be reduced to a ligand/ligand mixed-valent anion $[(Q^{2-})Cu^{II}(Q^{\bullet-})]^-$ with a typically broad and intense LLIVCT absorption (3) at around 1940 nm [41].

$$[(Q^{2-})Cu^{II}(Q^{\bullet-})]^- \xrightarrow[(NIR)]{h\nu} *[(Q^{-})Cu^{II}(Q^{2-})]^- \qquad (3)$$

Other non-innocent ligands such as azo-containing compounds [86] or α-diimines [87] were also shown to produce near-infrared absorptions from LLIVCT transitions if coordinated in different charge states to metal ions.

8. Summary

Based on examples and on the rationalization (Schemes 1 and 2) of how electronic transitions of sufficient intensity can occur in the NIR region for radical ions and for mixed-valent transition metal compounds it has been pointed out here that the combination of both approaches can lead to systems which cover the continuum between both alternatives and which exhibit intense NIR absorption bands at low energies. Whereas the group 10 metal bisdihiolate ions have already been well studied and applied [4,10,11], the non-innocent ligand bridged diruthenium compounds as discussed foremost in this article are less known despite their wide chemical variability (substitution, aggregation), stability, and their favorable optical properties [35,62–69]. It is quite likely that other classes of NIR absorbing coordination compounds will become available if NIR spectroscopy is becoming a more routine method in the characterization of new substances.

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